

GRAFT POLYMERIZATION OF VINYL MONOMERS ON TO ANIMAL SKINS *

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In previous communications¹⁻⁶ from this laboratory studies on the grafting of vinyl monomers on collagen powder and collagen solution were reported. The composition of graft copolymers was recognised to be a function of several factors such as catalyst concentration, monomer concentration, time and temperature and the physical condition of the collagen itself. The methods followed for grafting of vinyl monomers on collagen powder and collagen solution were found⁶ to be unsuitable for grafting on hides and skins which have a three-dimensional network structure. The accessibility of vinyl monomers to the interstices of the collagen fibres in the skin was very poor and methods were therefore worked out to improve this process and to bring about grafting. Because many of the vinyl esters have limited water solubility, an emulsion polymerization technique has a great practical significance. To facilitate easy penetration of monomers

the assistance of a penetrator and/or wetting agent as a transporter is of utmost importance and it is essential for the monomer to be grafted in the most complex structure of hide protein. Hence the aqueous emulsion technique was used for grafting on to goat pelts. Even though a number of emulsifiers were tried for the grafting of various vinyl monomers on goat skin pieces only a few emulsifiers gave satisfactory results. Anionic and nonionic surfactants when used alone did not give good results where a mixture of both was successful in grafting vinyl monomers to skin pieces. However, the choice of emulsifier for the synthesis of graft copolymers with the salts of Ce^{4+} is very limited.^{7,8} The emulsifier should not be oxidized by the Ce^{4+} .

Experimental

The grafting experiments were carried out on goat skins since they are thin and can withstand a greater degree of plumping than most of the other skins without damage to the fibre structure⁹. The soaking, liming (unhairing, fleshing etc.), deliming and bating were carried out by the conventional and standard

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methods. The skins were then pickled with acid and salt for a period of about 3-5 hours till the skins attained about pH of 2 — 2.5.

Grafting procedure

Vinyl monomers used for grafting on to goat pelts were methyl methacrylate (MMA), methylacrylate (MA), n-butylacrylate (n-BA) and acrylonitrile (AN). Graft copolymerisation was carried out by the ceric ion method, in which ceric ammonium sulfate (CAS) was used as the catalyst together with sulfuric acid and sodium sulfate.

The emulsion was prepared using a mixture of anionic and nonionic surfactants. The emulsifier was well stirred into water containing 5% sodium sulfate in a laboratory type blender. To this was added the vinyl monomer with continued stirring. The emulsion was then poured into a closed cylinder to which were added the delimed or pickled goat skin pieces and the mixture flushed with nitrogen. Then the required quantity of CAS solution in $1\text{N H}_2\text{SO}_4$ was added and well mixed. The pH of the solution was about 2.1. All the grafting experiments were carried out at room temperature (28–32°C). The reaction was allowed to continue overnight, after which the grafted pelts were thoroughly washed with water. Small pieces of the grafted samples were cut, dried and analysed for total nitrogen and arginine content. The percent grafting was calculated from these values as described in the previous papers. Since negligible amount of homopolymers was found to be extracted from the grafted pelts with the appro-

priate solvents for the homopolymers, no attempt was made to extract the homopolymers from grafted pelts prior to chrome tanning.

Chrome tanning

Since the grafting reaction was carried out in acid medium (pH 2.1) which is also the ideal condition for chrome tanning, the grafted pelts were not subjected to any further treatments and were directly chrome tanned by the conventional standard technique. Neutralization, dyeing and fatliquoring were carried out by the conventional methods.

The controls and experimentals were processed under identical conditions using the same bath and the properties of the final leathers were assessed.

Physical testing methods

Physical testing was done according to standard procedures. Tensile strength, percentage elongation, tear and stitch-tear strengths, water absorption, air permeability and water vapour permeability of the final leathers were determined according to standard procedures.

The shrinkage temperatures of the grafted pelts were determined in a Theis shrinkage temperature tester.¹⁰

Resistance of grafted pelts to mildew growth

In the present investigation the mildew resistance test was carried out in accordance with the ISI Specification,¹¹ without any preliminary leaching with water. The pieces of test materials (graft-

ed samples) as well as controls were dipped in distilled water using five times their weight for 5 minutes. They were allowed to drain and sprayed with the standard sand spore suspension. The test sand spore suspension contained the spores of *Aspergillus niger*, *A. flavus*, *A. terreus*, *A. nidulans*, *Paecilomyces varioti*, *Penicillium frequentans*, *P. rubrum*, *P. purpurogenum* species which have been found to grow on different types of pelts and leathers. Then the samples were suspended in humidity cabinet which maintained a relative humidity of 95–100% and a temperature of $30 \pm 1^\circ\text{C}$. The controls were given the same treatment with CAS and sulfuric acid as in the case of experimentals, but without any addition of monomer.

Results and Discussion

The leathers produced after grafting and their corresponding controls were assessed (Table 1) and their physical properties determined according to standard procedures. The physical properties of the two sides at corresponding areas were compared to give a reliable evaluation of the effect of the experimental treatment. The grafted skins were fuller and more resistant to mildew or fungus growth than the control skins. The leathers obtained from the grafted skins showed improved properties such as decreased water absorption, increased elongation, enhanced resistance to chemicals, improved light fastness of the dyed leathers and improved gloss of the resin finished leathers without detracting from the favourable properties of the natural leathers. Leathers obtained from grafted pelts showed an increase of

11–54% in thickness as compared to controls (Table 3). In Tables 3 and 4 are shown the various physical properties of the leathers after grafting and their corresponding controls. Even though the investigation was carried out on small pieces of pelt ($9'' \times 9''$) taken from matched paired sides (Fig. 1), further studies using full skins are necessary to establish more precisely the extent of changes in physical properties brought about by grafting. Such studies are in progress now. The data on the physical properties reported in this investigation may be taken only as the trend in changes of these properties in the leathers obtained after grafting with different polymers.

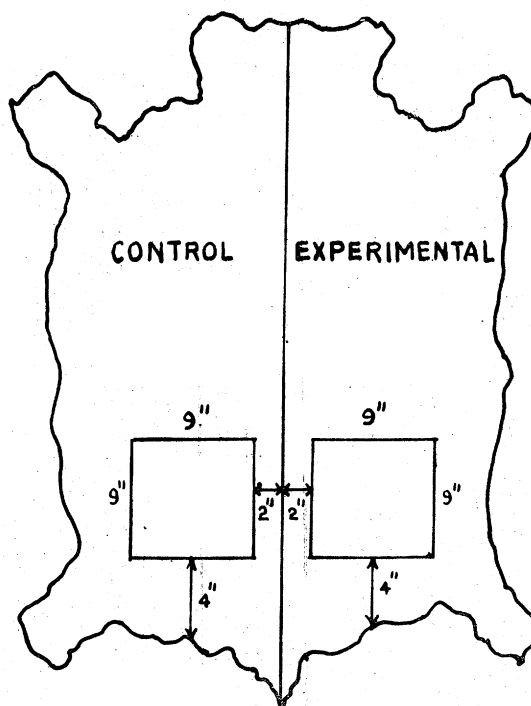


FIG. 1. Typical sampling method for matched pairs for experimental and control

Table 1

PHYSICAL CHARACTERISTICS OF THE GRAFTED AND TANNED PELTS

Monomer used for grafting	Percent grafting	Feel	Fullness	Smoothness	Crackiness	Dye affinity
Methylmethacrylate (MMA)	86.88	Slight tendency to hardening. Feel not affected	Very full	Slightly coarse	Does not crack	Good
Methylacrylate (MA)	75.84	Very slight ten- dency to harden- ing; feel not affected	Very full	Soft	Does not crack	Good
n-Butylacrylate (n-BA)	182.10	Very tacky (grain and flesh side)	Very full	Smoother	Does not crack	Good
Acrylonitrile (AN)	71.10	More tendency to hardening (grain hard)	Very full	Grain hard	Cracks slightly	Uneven

Table 2

SOME OF THE PROPERTIES OF HOMOPOLYMERS OBTAINED FROM VINYL MONOMERS USED IN GRAFTING EXPERIMENTS

Monomer	Tackiness	Hardness vs. Softness	Tensile strength	Elongation	Water absorption	Glass Transi- tion tempera- ture* T_g (C°)
Methylmethacrylate (MMA)	Tack-free	Fairly hard	High	Low	Low	105
Methyl acrylate (MA)	Almost tack-free	Fairly soft	Moderately high	Moderately high	Fairly high	3
n-Butyl acrylate (n-BA)	Very tacky	Very soft and plastic	Very low	Extremely high	Low	-56
Acrylonitrile (AN)	Tack-free	Fairly hard	High	Low	Low	104,130

*Data from L.E. Nielsen, Mechanical properties of Polymers, Reinhold, New York, 1965, pp. 19-23.

For convenience of presentation each physical property is discussed for all treatments together.

Tensile strength

The important properties of leather are hygienic and mechanical properties. The mechanical properties of leathers obtained from grafted skins are predictable to a certain extent from the properties of the polymeric side chains attached to the collagen backbone. The general properties of homopolymers obtained from the monomers used in the grafting experiments are summarised in Table 2. Adhesion properties of the polymer branches attached to the backbone appear to have a considerable effect on the macro-structure of the leather and on its mechanical properties. The values for the tensile strength of the variously grafted and chrome tanned goat pelts (Table 3) along with the values for cor-

responding controls show that appreciable changes in tensile strength occur only in the cases of polyacrylonitrile (PAN) and polybutylacrylate (PBA) grafted samples. The leathers obtained after grafting with PBA showed a significant increase in the tensile strength whereas the leathers obtained from the PAN grafted skin showed a significant decrease. The difference in the results in these two cases may be attributed to the fact that PBA is a soft film forming polymer, while PAN is a polymer which is particulate in nature. Hence when a tensile force is applied, the film formation on the fibres in the case of PBA may prevent easy slippage of fibres past one another resulting in an increase in tensile strength. It was also reported that the tensile strength of the leather increased with increased adhesion of the polymer to the collagen fibre although hardness of the film was decreasing.¹² In

Table 3

PHYSICAL TEST DATA FOR GOAT PELTS GRAFTED WITH VARIOUS VINYL POLYMERS AND CHROME TANNED

Sample	Percent** grafting	Air per- meability sec.	Tongue tear resistance kg/per/cm thickness	Tensile strength kg/sq.cm.	Elongation Percent at break	Stitch tear resistance kg/cm thickness	% average gain in thickness
Control*	—	86	12.6	134.5	75	64.5	—
PMMA grafted and chrome tanned	86.88	92	11.9	150.3	62.5	40.1	+11.10
Control*	—	85	37.1	202.7	75	—	—
PMA grafted and chrome tanned	75.84	50	22.1	170.2	68.7	—	+54.50
Control*	—	83	13.6	144.4	68.7	90.9	—
PBA grafted and chrome tanned	182.10	1215	22.7	209.7	131.2	68.1	+26.45
Control*	—	49	13.3	179.9	62.5	60.6	—
PAN grafted and chrome tanned	71.10	50	9.5	100.5	43.7	56.8	+17.65

*Directly chrome tanned

**Calculated from nitrogen analysis or arginine estimation.

the case of PAN grafted skins the particles formed may prevent the reorientation of the fibre network and such obstruction to reorientation is known to decrease the tensile strength, polymethyl methacrylate (PMMA) grafted skins, unlike PAN grafted samples, did not show any decrease in tensile strength. Even though PAN and PMMA are hard polymers having high glass transition temperatures (T_g), the stiff-film forming PMMA may cause to some extent cementing of the fibres.¹³ This may explain the difference in behaviour of PMMA grafted skin as compared to PAN grafted skin, with respect to tensile strength.

Elongation at break

The butylacrylate grafted samples are of much interest in that the elongation was increased two-fold without a decrease in tensile strength (Table 3). Very little change was observed in other cases, all values except in the case of PBA were below the respective control leathers (Table 3). From Table 3, it can be seen that the elongation at break in the case of PAN grafted sample is significantly lower than that of PMMA and polymethylacrylate (PMA) grafted samples. The increased extension of leathers modified with PBA may be explained by the variation in elastic properties of the collagen material arising from the grafting of a flexible chain polymer with a low glass transition point. In the case of PAN grafted sample the particles formed may prevent the reorientation of the fibre network and hence the skin

may not be allowed to elongate much before break.

Tongue-tear and stitch-tear strengths

In general a decrease in tear strength was observed in all the cases of grafted samples (Table 3). The mechanism of tear involves at least partly cutting of fibres along the diameter and hence the intrinsic strength of the fibres is involved. It is known¹⁴⁻¹⁶ that grafting with the polymers employed in this investigation may result in breakage of hydrogen bonds and salt linkages in proteins, which may weaken the fibres resulting in reduced tear strengths. However, PBA grafted sample showed a slight increase in tongue-tear strength even though there was no corresponding increase in the stitch tear strength in this treatment (Table 3). The reason for this behaviour of PBA grafted sample is not very clear.

Water absorption

Many methods have been directed to the end of obtaining increased water resistance to leathers but only with partial success. To overcome the hydrophilic character of the hide collagen grafting of synthetic polymers like PMMA, PBA and PAN was found to be beneficial. The treatment caused a drastic decrease in water absorption and the extent of water absorption was found to vary according to the hydrophobic character of the polymer grafted (Table 4). From Table 4, it can be seen that after 24 hours immersion the percent decrease in water absorption was highest in the case of PMMA grafted

Table 4

PHYSICAL TEST DATA FOR LEATHERS OBTAINED FROM TREATED AND UNTREATED SKINS—BEHAVIOUR TO WATER ABSORPTION

Nature of treatment	Percent grafting	Water vapour permeability mg/sq.cm/hr	% Water absorption			% decrease in water in absorption
			1½ hr	2 hr	24 hr	
Goat skin straight chrome tanned	—	9.9	201.4	201.4	238.6	40.78
Goat skin grafted with PMMA and chrome tanned	86.88	6.5	128.4	128.4	141.3	
Goat skin straight chrome tanned	—	8.1	209.7	222.5	273.3	2.196
Goat skin grafted with PMA and chrome tanned	75.84	9.4	218.7	243.0	267.3	
Goat skin straight chrome tanned	—	8.4	189.8	189.8	195.3	26.42
Goat skin grafted with PBA and chrome tanned	182.10	5.1	124.8	132.4	143.7	
Goat skin straight chrome tanned	—	10.4	225.1	225.1	253.2	28.47
Goat skin grafted with PAN and chrome tanned	71.10	6.9	163.8	163.8	181.1	

and lowest in the case of PMA grafted and had intermediate values with PBA and PAN grafted samples. This can be explained on the basis of the hydrophobic nature of the polymers grafted: PMMA is most hydrophobic, PMA is least hydrophobic while PBA and PAN occupy intermediate positions.

Water vapour permeability

Another very valuable property of the leather is its excellent hygienic property such as water vapour permeability. Therefore, when grafting pelts with vinyl polymers, one must bear in mind retaining these hygienic properties to the greatest possible extent whilst obtaining full utilisation of improvements in the physical properties by graft copolymerisation. The permissible amount of polymer to be grafted may be determined based on the hygienic properties of leather such as water vapour permeability and/or the leather properties such as tear strength etc. Water vapour permeability is usually regarded as a key property in developing a leather-like structure.¹⁷ It is particularly desired for shoe uppers, and together with moisture absorption, is a factor in comfort of shoes to the wearer. In general, leather absorbs more water vapour than synthetic shoe materials.

Water vapour permeability data on grafted leathers and controls are given in Table 4. From Table 4, it is seen that 86% of grafted PMMA and 70% of grafted PAN, both reduce the permeability from 9.9 to 6.5 and 10.4 to 6.9 mg/sq.cm./hr. 76% of grafted PMA shows a little increase from 9.4 to 10.4

whereas in the case of PBA (182%) it decreases from 8.4 to 5.1 mg./sq.cm./hr. The reduced values obtained after grafting are considered ample for comfort of shoe upper leather. Generally the water vapour permeability of leathers¹⁸ usable for shoe uppers is between 1 to 10 mg/sq.cm./hr. and all the grafted leathers have permeabilities in the middle of this range. The hygienic properties are still provided by the high content of collagen fibres even after grafting with synthetic polymers. The general decrease in water vapour permeability observed in most cases may be attributed to a constriction of the passages through which the vapour passes and to the coating of the fibres with polymer which prevents migration of absorbed water through the fibres by a wick-like action.

Air permeability

The concept of leather breathing is not a characteristic that distinguishes it from synthetic materials and air permeability on the other hand does not seem to be a significant comfort factor.¹⁷ The leathers obtained from PMMA and PAN grafted skins retained almost the same permeability (Table 3) for air as in the case of their corresponding controls. There was a slight increase in the air permeability for the PMA grafted sample and a very significant decrease in air permeability was observed for PBA grafted sample as compared to controls (Table 3). The low permeability in the case of PBA grafted sample may be attributed to the elastomeric tacky nature of these grafted samples and to the high degree of grafting achieved. It is well known that softer elastomeric polymers

Table 5

VARIATION IN SHRINKAGE TEMPERATURE WITH PERCENT GRAFTING OF PMMA ON GOAT PELTS

Time of grafting (hr)	Percent grafting	Shrinkage Temperature (T _s) °C.
1	21.19	50
2	30.67	60
3	57.65	60
24	143.10	71
Control untreated	—	56

tend to give impermeable though tougher structures on precipitation from solutions. It was also observed that the water vapour permeability of PBA grafted leathers has the lowest value when compared to other grafted samples.

Shrinkage temperature

The collagen fibres when heated in contact with water contract sharply at a certain temperature, known as the shrinkage temperature. In the molecular model, this has been pictured as a breakdown of the stable parallel orientation of molecular chains in the fibres due to the destruction of the cohesive bonds between the fibres and the subsequent coiling up of the molecules. The

shrinkage temperature should therefore decrease with the decrease in cohesion between molecules and increase with the increase in cohesion. Hence chemical reagents known to disrupt hydrogen bonding have a profound effect in reducing the shrinkage temperature of collagen. In general, grafting is known to reduce the extent of hydrogen bonding between polypeptide,^{15,16} chains.

Table 5 shows the shrinkage temperature (T_s) of goat pelts grafted with different amounts of PMMA. From the table, it can be seen that the T_s is less when the percent grafting is low (at about 20% grafting) while it increases at higher percentages. The lower value obtained may be attributed to the brea-

Table 6

SHRINKAGE TEMPERATURE OF PELTS GRAFTED WITH DIFFERENT POLYMERS

Type of monomer	Percent grafting	Shrinkage temperature (T _s) °C.
MMA	86.88	68
MA	75.84	56
n-BA	182.10	57
AN	71.10	67
Control untreated	—	56

kage of hydrogen bonds. When more polymer is forced into the matrix, the collagen graft copolymer system becomes more hydrophobic and even though hydrogen bond breakage occurs at these higher percentages also, the effect of the hydrophobic nature of the polymer becomes more predominant and hence with decreased water absorption capacity the T_g increases.

Shrinkage temperatures of the goat pelts grafted with different polymers are shown in Table 6. The higher T_g values observed for PMMA and PAN grafted skins may be attributed to the hydrophobic nature of the polymers and their greater mechanical hardness (high glass transition temperatures). The increase in shrinkage temperature in the case of PAN may also be due to the high negative polarity and small size of the $-C \equiv N$ group, together with the readily available hydrogen atoms for hydrogen bonding¹⁹ in the $-CH_2-CHCN$ units. As compared

to the PMMA and PAN grafted pelts, PBA and PMA grafted pelts did not show any appreciable increase in T_g . In these two cases the dimensional shrinkage is perhaps facilitated by the lower glass transition temperatures (PMA, PBA) and the hydrophilic nature (PMA) of these polymers.

Resistance of grafted pelts to mildew growth.

The results obtained on the development of mildew on grafted goat pelts are shown in table 7 and fig. 2. The results show that grafting of vinyl polymers on pelts bestows a

certain amount of resistance to the pelts against mildew growth. Grafting with PMMA was associated with maximum resistance to the development of mildew, since only very negligible (+) growth was seen in this sample as compared with the extensive growth of mildew in the control samples at the end of 30 days test period. PAN grafted samples were also fairly resistant (++) but PBA and PMA grafted samples were less resistant (+++). In the order of decreasing resistance to mildew attack the various grafted pelts could be arranged in the order $PMMA > PAN > PBA > PMA$. The fungal growth actually started after two days on the control and a heavy growth was observed after six days, whereas the grafted

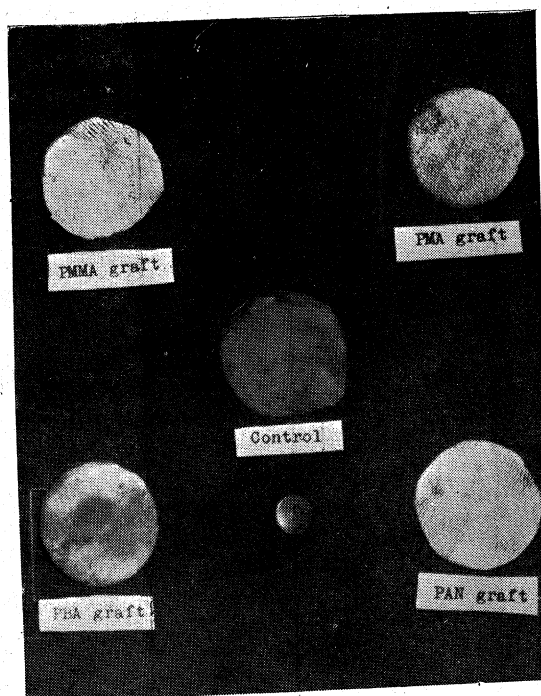


FIG. 2. Extent of mold growth on grafted and control pelts during the period of 30 days

desirable that a leather finish be formulated to yield a gloss which does not change upon plating. Superior properties of the finished leather will be obtained with the materials which adhere better to leather since the gloss is primarily a function of a film continuity and the compatibility of the components. If a vinyl polymer is

ing the course of this work.

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PERIOD OF 30 DAYS	period, (days)	30	+	+	+	+	+
		14	+	+	+	+	+

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